MEAN AMPLITUDES OF VARIATION, BASTIANSEN-MORINO SHRINKAGE EFFECT AND MOLECULAR POLARIZABILITIES FOR THE DIHALIDES OF SOME GROUP IIA ELEMENTS

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ABSTRACT. A brief survey of the vibrational and dimensional analysis is given for the gaseous dihalides of some group IIA elements possessing a linear symmetrical structure with the symmetry point group $D_{\infty h}$. The transferability of vibrational frequencies among related molecules is discussed. Mean-square amplitude quantities, generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes and mean cross products) and mean amplitudes of vibration for the bonded as well as nonbonded atom pairs have been evaluated by the Cyvin method utilizing symmetry coordinates at the temperatures T = 500°K, T = 1000°K and T = 1500°K. The values of Bastiansen-Morino shrinkage effect have been computed at these temperatures. The bond and molecular polarizabilities have also been calculated by the Lippincott-Stutman method employing the delta-function model of chemical binding. The calculated values of the molecular polarizabilities are in good agreement with the available experimental ones.

INTRODUCTION

The dihalides of group IIA elements were for many years subjected to several vibrational and structural investigations in deciding whether they have a linear configuration with the symmetry point group $D_{\infty h}$ or a bent one with the symmetry point group C_{2v}. However, the recent investigations have very categorically confirmed that these metal dihalides possess only a $D_{\infty h}$ symmetry and not a C_{2v} one. It is aimed here to evaluate the mean amplitudes of vibration and Bastiansen-Morino shrinkage effect for these dihalides with help of the recent vibrational and structural data by the Cyvin method (1959) at the temperatures T = 500°K, T = 1000°K and T = 1500°K with a view that the results of the present investigation would be very helpful for the interpretation of the results of electron diffraction studies. Lippincott and Stutman (1964) recently applied the delta-function potential model to the calculation of bond and molecular polarizabilities of various diatomic and polyatomic molecules having their elements only from and beyond the IVA-group of the periodic table and their results are in good agreement with the experimental ones obtained from molar refractions, dielectric constants etc. through the well-known relations such as Langevin-Debye

and Lorentz-Lorentz equations. Such a model has not been so far applied to molecules having their elements from below the IVA-group and B-group of the periodic table. In the way of further testing the accuracy of the delta-function model of chemical binding, it is also aimed here to calculate the bond and molecular polarizabilities for the dihalides and compare the calculated molecular polarizabilities with the available experimental values.

VIBRATIONAL AND STRUCTURAL ANALYSIS

Braune and Knocke (1933), Gregg *et al* (1937) and Akishin *et al* (1957, 1958) confirmed from their electron diffraction studies a linear symmetrical structure for the dihalides of the second group elements. Warton *et al* (1963) recently explained by the deflection of beams of alkaline-earth halides by inhomogeneous electric fields that barium halides, strontium fluoride, strontium chloride and calcium fluoride have permanent electric dipole moments, which implies that they do not have a center of symmetry. No polarity was observed for the higher members of calcium and strontium families. This observation is most naturally interpreted as implying a non-linear equilibrium geometry. The general trend found in the alkaline-earth dihalides was that large metal atoms and small halogens favoured a rather bent configuration. Later, Buchler *et al* (1964) re-examined the deflection of mass spectrometrically detected beams of the fluorides and chlorides of many metals and found that all were nonpolar except calcium fluoride thereby lending support to the results of earlier electron diffraction studies (1933, 1937, 1957, 1958) as well as vibrational and electronic spectral studies (1964).

The vibrational frequencies, molecular structure and molecular weight yield to the calculation of the vibrational, rotational and translational contributions to the free energy functions of the gaseous molecules. Where sufficient vibrational data is unavailable for a molecular system, vibrational frequencies from related molecules having similar chemical bonds may be substituted, or the frequencies lacking may be estimated from force constants of related molecules by employing a suitable potential energy function. In cases of simple triatomic molecules, the vibrational frequencies may well be evaluated from the frequencies observed for related diatomic molecules by using a suitable valence force model. The values of the free energy functions thus calculated spectroscopically may be compared with those of the experimental ones. Several investigators have successfully applied this method for many molecules and a detailed account has been given by Nagarajan (1964). Following this method and with help of the available spectroscopic data cited above (1964), Brewer *et al* (1963) evaluated the unassigned fundamental frequencies for the dihalides of beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, tin, and lead by the process of transferring the characteristic frequencies, force constants and internuclear distances from related molecules having similar chemical bonds, calculated the free energy func-

tions and compared them with those experimentally observed. On the basis of the principle postulated by Cyvin (1959), the mean amplitudes of vibration and Bastiansen-Morino shrinkage effect were evaluated by Nagarajan (1964) for these molecules except for the dihalides of calcium, strontium and barium by using the vibrational and structural data described above. The fundamental frequencies in cm^{-1} and internuclear distances in A for the dihalides of calcium, strontium and barium are, in accordance with the recent vibrational and structural studies cited above, given in Table I.

MEAN AMPLITUDES OF VIBRATION

A linear symmetrical triatomic molecule i –j –i possessing the symmetry point group $D_{\infty h}$ gives rise, according to the relevant symmetry considerations and selection rules (1960), to four vibrational degrees of freedom constituting only three fundamental frequencies under the various irreducible representations as follows $\Sigma_g^+ + \pi_u + \Sigma_u^+$ where the gerade mode is Raman active only and symmetric with respect to the center of symmetry while the ungerade modes are infrared active only and asymmetric with respect to the center of symmetry. The frequency ν_1 corresponds to a totally symmetrical stretching mode under the symmetry species Σ_g^+ ν_2 to a bending mode under the species π_u and ν_3 to an asymmetrical stretching mode under the species Σ_u^+. The vibrations coming under the species Σ_g^+ and Σ_u^+ are nondegenerate and parallel vibrations while the remaining under the species π_u is a doubly degenerate and perpendicular one. A schematic representation of the normal modes of oscillation for a molecule of the present study has already been given by Herzberg (1960).

Cyvin (1959) was, in the analysis of molecular vibrations, the first to introduce the symmetry coordinates into the evaluation of mean-square amplitudes of vibration. On the basis of the principle postulated by Cyvin (1959), a theory for the determination of mean-square amplitudes of vibration for a molecule of the present study has already been developed by Cyvin himself (1959, 1960) and applied to may molecules. The same method has been adopted here and one may refer to Cyvin (1959 1960) for the detailed theoretical considerations and calculations. The secular equations giving the normal frequencies in terms of the mean-square amplitude quantities were constructed with help of the fundamental frequencies and internuclear distances in wave numbers and Angstrom units given in Table I and Σ and G matrices at the temperatures T - 500°K, T - 1000°K and T — 1500°K for the dihalides of calcium, strontium and barium. Since all the experiments will be done only at very high temperatures, the secular equations were constructed here above 500°K. Since the secular equation is, on account of the greater symmetry of the molecular system, singular under every symmetry species, the three fundamental frequencies are well sufficient to evaluate the three vibrational constants, namely, Σ_{11}, Σ_{22} and Σ_{33}. From those three symetrized mean-square amplitude matrices, the mean-ssquare amplitude quantities were

calculated and their values in Å^2 are given in Table II for all the molecules studied at the temperatures T = 500°K, T = 1000°K and T = 1500°K where σ_r is the mean-square amplitude quantity due to the bonded atom pair i-j σ_{rr} the quantity due to the interaction of the bonded atom pairs and σ_θ the quantity due to the bending of the molecule The generalized mean-square amplitude quantities (mean-square parallel amplitudes $<\Delta z^2>$, mean-square perpendicular amplitudes $<\Delta x^2>$ and $<\Delta y^2>$ and mean cross products $<\Delta x \Delta y>$, $<\Delta y \Delta z>$ and $<\Delta z \Delta x>$ are given in Table III in Å^2 for the bonded as well as nonbonded atom pairs at the temperatures T = 500°K, T = 1000°K and T = 1500°K. The corresponding calculated values of the mean amplitudes of vibration in Å are given in Table IV at the three temperatures for the bonded and nonbonded distances.

The mean-square amplitude of vibration due to the bending of the molecule is in general very much greater than that due to the bonded atom pair and the quantity due to the interaction of the bonded atom pairs is negligibly small in many cases (see Table II). By symmetry of the molecular system, the mean-square perpendicular amplitudes of vibration for the bonded atom pair and the mean cross products for the bonded as well as nonbonded atom pairs become vanished. Hence the mean cross products are not listed in Table III.

The mean amplitude of vibration for the nonbonded atom pair is in general greater than that of the bonded atom pair for all the molecules (see Table IV). This shows that larger the distance between the atoms greater will be the value for the mean amplitude of vibration. Further, the mean amplitude of vibration for the bonded as well as nonbonded atom pairs are in the increasing order at any temperature toward the higher members in the halogen series of the elements studied. This evidently shows that the replacement of end atoms with atoms of higher atomic weight to the molecular system causes a decrease in the fundamental frequencies (see Table I) and an increase in the mean amplitudes of vibration for the bonded and nonbonded distances. The situation is reversed in the cases of corresponding force constants Though the electron diffraction studies were made for all the molecules studied, the values of mean amplitudes of vibration were not reported such that a comparison could be made here. However, the results of the present investigation would be very useful for the interpretation of the results of electron diffraction studies when undertaken again for these molecules.

BASTIANSEN-MORINO SHRINKAGE EFFECT

The distance between the oxygen atoms in carbon dioxide observed from electron diffraction studies by Karle and Karle (1949) was not exactly twice the value for the carbon-oxygen distance but less. The apparent shortening or shrinkage of the longer distances in several linear chains of atoms was observed by Bastiansen *et al* (1956, 1960) and the effect was confirmed as due to the out-of-linearity vibrations. A theory has been established by Morino (1960) for

this effect in terms of intramolecular motions using the generalized mean-square amplitudes (1955). The theory is based on a power series expansion for the shrinkage effects of linear as well as non-linear conformations as developed by Morino *et al* (1962) and Cyvin (1961 1962). In the case of a linear conformation, the shrinkage is mainly due to the perpendicular displacements of the nuclei and the anharmonic terms are cancelled. In the case of a non-linear conformation, two kinds of shrinkages have been defined viz., the "natural" and "practical" shrinkages. They are shown to be identical to the first order approximation (1961, 1962). The anharmonic terms, in contrast to the linear conformations, may not necessarily be cancelled out in the non-linear conformations except for highly symmetrical molecules having no totally symmetrical bonding modes in the ground electronic states Later, the name, "Bastiansen-Morino Shrinkage Effect" has been intro- duced on this aspect by many investigators (1965) in their spectroscopic calcula- tions

An analytical expression for the mean value of an arbitrary internuclear distance r_{ij}^g obtained from electron diffraction studies for an atom pair i j can simply be related to the equilibrium distance r_{ij}^e in terms of the mean-square perpendicular amplitudes of vibration as follows .

$$r_{ij}^g = <r_{ij}> = r_{ij}^e + <\Delta z_{ij}> + (1/2r_{ij}^e)(<\Delta x_{ij}^2> + <\Delta y_{ij}^2>)$$

where $<\Delta z_{ij}>$ is the so-called anharmonic term which will be vanished when purely harmonic vibrations alone are considered. The Bastiansen-Morino shrinkage effect for a molecule of the present investigation is given by taking the difference of r_{ij}^g minus the sum of the individual bond lengths r_{ij}^g and r_{ji}^g composing it .

$$\delta = r_{ii}^g - (r_{ij}^g + r_{ji}^g) \quad r_{ii}^g \quad 2r_{ij}^g - \quad 2 \cdot \Delta x_{ij}^2 / r_{ij}^e$$

where the mean-square prependicular amplitudes of vibration $<\Delta x_{ii}^2>$ and $<\Delta y_{ii}^2>$ for the nonbonded atom pair i . i are vanished by symmetry of the molecular system and the mean-square perpendicular amplitudes of vibration $<\Delta x_{ij}^2>$ and $<\Delta y_{ij}^2>$ are identical for the bonded atom pair i j. The shrinkage begins mainly with the second order terms in the expression for the Bastiansen-Morino shrinkage effect as the linear term completely vanishes. The calculation for the Bastiansen-Morino shrinkage effect needs the values of the mean-square prependicular amplitudes of vibration and internuclear distances at the equilibrium configuration. High precision values of the inter-nuclear distances at the equilibrium configuration are not required for such calculation. However, approximate values of the internuclear distances obtained from other sources such as microwave, x-ray diffraction or infrared absorption studies will quite be sufficient as the second order terms are only the correction terms.

Using the internuclear distances in Å given in Table I and the mean-square perpendicular amplitudes of vibration in Å^2 given in Table III, the Bastiansen-Morino shrinkage effects at the temperatures T = 500°K T = 1000°K and T = 1500°K where calculated and their values in Å are given in Table V for all the molecules studied The shrinkage effects, as in the cases of mean amplitude of vibration, are in the increasing order toward the higher members of the halogen group of the calcium strontium and barium families. Though these values appear small in magnitude, they are real. These are to be added at the appropriate temperatures to those of the observed nonbonded distances from electron diffraction experiments in order to obtain the actual values at the equilibrium configuration, thereby compensating the apparent shortening in the internuclear distances.

MOLECULAR POLARIZABILITIES

In order to test how far the polarizability could be a useful criterion for testing the accuracy of wave functions adopted, many investigations in recent years have been made and developed in several ways to compute the atomic and molecular polarizabilities on the basis of quantum mechanical models for many molecules and ions. Of the various potential models so far developed, the most recent one is the delta-function potential model initiated by Frost (1954 1955, 1956) and developed by Lippincott (1955 1957). Recently, Lippincott and Stutman (1964) applied this semi-empirical model to develop a method of generating component polarizabilities in order to compute the molecular or average polarizabilities. This model gives explicit expressions for the parallel and perpendicular components and mean polarizabilities for diatomic as well as polyatomic molecules having their elements only from and beyond the IVA-group of the periodic table. The molecular polarizability is composed mainly of the bond parallel components obtainable from molecular delta-function model and bond perpendicular components obtainable from the atomic delta-function polarizabilities. The polarizability contributions from the bond region electrons and those from the nonbond region electrons have been clearly distinguished. In addition, corrections to the parallel and perpendicular components are made to compensate for polarity effects. The same method has been adopted for the dihalides of beryllium, magnesium, calcium strontium and barium to compute the bond and molecular polarizabilities and one may refer to Lippincott and Stutman (1964) for the detailed theoretical considerations and computations.

The delta-function strengths A's in atomic units, atomic polarizabilities α's sin 10 ^{25} cm^3 and c's in atomic units were, according to Lippincott and Dayhoff (1960) and Lippincott and Stutman (1964), derived and their values are given as follows : $A_{Be} = 0.538$, $A_{Mg} = 0.414$, $A_{Ca} = 0.337$, $A_{Sr} = 0.319$, $A_{Ba} = 0.289$, $A_F = 1.065$, $A_{Cl} = 0.753$, $A_{Br} = 0.633$, $A_I = 0.584$, $\alpha_{Be} = 38.02$, $\alpha_{Mg} = 83.70$, $\alpha_{Ca} = 154.76$, $\alpha_{Sr} = 182.42$, $\alpha_{Ba} = 245.84$, $\alpha_F = 4.90$, $\alpha_{Cl} = 13.88$ $\alpha_{Br} = 19.41$,

$\alpha_I = 29.72$, $c_{Be} = 1.522$, $c_{Mg} = 1.434$, $c_{Ca} = 1.35$, $c_{Sr} = 1.427$, $c_F = 5.635$, $c_{Cl} = 4.88$, $c_{Br} = 4.737$ and $c_I = 4.886$ From the electron diffraction studies by Akishin *et al* (1957, 1958), the following values of the internuclear distances in Å were used here for the dihalides of beryllium and magnesium 1.40 for Be—F, 1.75 for Be—Cl, 1.91 for Be-Br 2.10 for Be -I, 1.77 for Mg F 2.18 for Mg—Cl, 2.34 for Mg -Br 2.52 for Mg- -I. The internuclear distances for other dihalides were used from Table I.

TABLE I

Fundamental frequencies in cm^{-1} and internuclear distances in Å for the dihalides of some group IIA elements.

Molecule	$\nu_1(\Sigma_g^+)$	$\nu_2(\pi_u)$	$\nu_3(\Sigma_u^+)$	r
CaF_2	484	95	675	2.10
$CaCl_2$	268	63	446	2.51
$CaBr_2$	164	52	367	2.67
CaI_2	118	45	321	2.88
SrF_2	454	77	543	2.20
$SrCl_2$	254	48	342	2 67
$SrBr_2$	156	37	262	2 82
SrI_2	111	31	219	3 03
BaF_2	439	70	496	2.32
$BaCl_2$	248	43	302	2 82
$BaBr_2$	154	32	226	2 99
BaI_2	109	26	184	3 20

TABLE II

Mean-square amplitude quantities in $Å^2$ for the dihalides of some group IIA elements.

Molecule	Symbol	Mean-square amplitude quantity		
		T 500 K	T 1000 K	T 1500°K
CaF_2	σr	0 0032176	0 0055453	0 0081942
	σrr	−0 0001936	−0 0000939	0 0000815
	$\sigma\theta$	0 2616924	0 5208368	0 7286038
$CaCl_2$	σr	0 0050031	0 0094965	0 0139979
	σrr	0 0002245	−0 0000445	- 0 0002704

TABLE II (*contd.*)

Molecule	Symbol	Mean-square amplitude quantity		
		T 500°K	T 1000°K	T 1500°K
	$\sigma_{\perp}$	0.4658179	0.9414614	1.3941088
	σ_{l}	0.0056859	0.0110253	0.0161107
$CaBr_2$	σ_{rr}	0.0002223	0.0002519	0.0000071
	$\sigma_{\perp}$	0.5475689	1.0125188	1.6869917
	σ_{l}	0.0068722	0.0137669	0.0207138
CaI_2	σ_{rl}	−0.0001852	0.0003382	0.0003271
	$\sigma_{\perp}$	0.7226042	1.4438660	1.9489571
	σ_{l}	0.0035048	0.0064617	0.0091216
SrF_2	σ_{rr}	0.0000852	0.0001020	0.0000929
	$\sigma_{\perp}$	0.3016469	0.6064996	0.9588259
	σ_{r}	0.0054142	0.0103934	0.0157682
$SrCl_2$	σ_{rl}	0.0001249	0.0001210	−0.0000900
	$\sigma_{\perp}$	0.5130009	1.0043116	1.3746590
	σ_{r}	0.0062587	0.0122298	0.0179449
$SrBr_2$	σ_{rr}	−0.0000115	0.0001164	0.0003521
	$\sigma_{\perp}$	0.6447195	1.1512319	1.6106553
	σ_{r}	0.0075913	0.0151840	0.0233595
SrI_2	σ_{rl}	−0.0000645	−0.0001895	0.0006004
	$\sigma_{\perp}$	0.7686537	1.5366728	2.3382931
	σ_{r}	0.0036807	0.0066716	0.0097318
BaF_2	σ_{ll}	−0.0000599	0.0000543	0.0000316
	$\sigma_{\perp}$	0.3247989	0.6479921	0.9445528
	σ_{r}	0.0056936	0.0108984	0.0163300
$BaCl_2$	σ_{rr}	−0.0001384	−0.0001298	−0.0002725
	$\sigma_{\perp}$	0.5596818	1.1183238	1.6772341
	σ_{r}	0.0063352	0.0126196	0.0190220
$BaBr_2$	σ_{rr}	−0.0000068	−0.0001132	0.0005841
	$\sigma_{\perp}$	0.6424226	1.2841889	2.1401817
	σ_{r}	0.0078850	0.0155887	0.0236551
BaI_2	σ_{rr}	−0.0002018	−0.0003191	0.0007444
	$\sigma_{\perp}$	0.8977888	1.4555268	2.4742529

TABLE III

Generalized mean-square amplitude quantities in Å² for the dihalides of some group IIA elements.

Molecule	Mean-square amplitude quantity	$i-j$			$i-i$		
		T = 500°K	T = 1000°K	T = 1500°K	T = 500°K	T = 1000°K	T = 1500°K
CaF_2	$\langle \Delta z^2 \rangle$	0 0032176	0.0055453	0 0081942	0 0064352	0 0110906	0 0163884
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 0654321	0.1302092	0.1821509	0	0	0
$CaCl_2$	$\langle \Delta z^2 \rangle$	0 0050031	0 0094965	0 0139979	0 0100062	0 0189930	0 0279958
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 1164545	0 2353654	0 3485272	0	0	0
$CaBr_2$	$\langle \Delta z^2 \rangle$	0 0056859	0.0110253	0.0161107	0 0113718	0 0220506	0 0322214
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 1368922	0 2531297	0.4217479	0	0	0
CaI_2	$\langle \Delta z^2 \rangle$	0 0068722	0 0137669	0 0207138	0 0137444	0.0275338	0 0414276
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 1806511	0 3609665	0 4872393	0	0	0
SrF_2	$\langle \Delta z^2 \rangle$	0 0035048	0.0064617	0 0091216	0 0070096	0.0129234	0.0182432
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 0754117	0.1516249	0 2397065	0	0	0
$SrCl_2$	$\langle \Delta z^2 \rangle$	0 0054142	0.0103934	0 0157682	0 0108284	0.0207868	0 0312524
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 1282502	0.2510779	0 3436648	0	0	0

TABLE III—(*contd*).

Molecule	Mean-square amplitude quantity	$i-j$			$i-i$		
		T = 500°K	T = 1000°K	T = 1500°K	T = 500°K	T = 1000°K	T = 1500°K
$SrBr_2$	$\langle \Delta z^2 \rangle$	0 0062587	0 0122298	0 0179449	0 0125174	0.0244596	0 0358898
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0.1611799	0 2878080	0.4026638	0	0	0
SrI_2	$\langle \Delta z^2 \rangle$	0 0075913	0 0151840	0 0233595	0 0151826	0 0303680	0 0467190
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0 1921634	0.3841682	0 5845733	0	0	0
BaF_2	$\langle \Delta z^2 \rangle$	0.0036807	0.0066716	0 0097318	0.0073614	0 0133432	0 0194636
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0.0811997	0 1619980	0 2361382	0	0	0
$BaCl_2$	$\langle \Delta z^2 \rangle$	0.0056936	0.0108984	0 0163300	0 0113872	0.0217968	0 0326600
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0.1399250	0.2795810	0.4193085	0	0	0
$BaBr_2$	$\langle \Delta z^2 \rangle$	0.0063352	0 0126196	0.0190220	0 0126704	0 0242392	0 0380440
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0.1606056	0.3210472	0 5350454	0	0	0
BaI_2	$\langle \Delta z^2 \rangle$	0 0078850	0.0155887	0.0236551	0 0157700	0 0311774	0.0473102
	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	0.2244472	0 3638817	0.6185632	0	0	0

TABLE IV

Mean amplitudes of vibration in Å for the dihalides of some group IIA elements.

Molecule	Distance	Mean amplitude of vibration		
		T = 500°K	T = 1000°K	T = 1500°K
CaF_2	Ca-F	0.0567	0 0745	0.0905
	F F	0 0802	0 1052	0.1280
$CaCl_2$	Ca-Cl	0.0707	0 0974	0 1183
	Cl—Cl	0 1000	0 1378	0 1673
$CaBr_2$	Ca-Br	0 0754	0.1051	0.1270
	Br--Br	0 1066	0 1485	0.1795
CaI_2	Ca-I	0 0829	0 1173	0.1439
	I—I	0 1172	0.1659	0.2035
SrF_2	Sr-F	0 0592	0 0804	0.0955
	F --F	0 0834	0 1137	0.1351
$SrCl_2$	Sr-Cl	0 0736	0 1020	0.1256
	Cl—Cl	0 1041	0 1442	0.1776
$SrBr_2$	Sr-Br	0 0791	0 1106	0.1340
	Br--Br	0 1119	0 1564	0.1894
SrI_2	Sr-I	0 0872	0 1232	0.1529
	I—I	0 1232	0 1743	0.2162
BaF_2	Ba-F	0 0607	0 0817	0.0987
	F—F	0 0858	0 1155	0.1395
$BaCl_2$	Ba-Cl	0.0755	0 1044	0.1277
	Cl—Cl	0.1068	0 1477	0.1807
$BaBr_2$	Ba-Br	0 0796	0.1124	0.1379
	Br—Br	0 1126	0 1557	0.1951
BaI_2	Ba-I	0.0888	0.1248	0.1538
	I—I	0.1256	0.1766	0.2175

TABLE V

Bastiansen-Morino shrinkage effect in Å for the dihalides of some group IIA elements.

Molecule	Bastiansen-Morino shrinkage effect		
	T = 500°K	T = 1000°K	T = 1500°K
CaF_2	0.06231	0.12401	0.17348
$CaCl_2$	0.09280	0.18754	0.27771
$CaBr_2$	0.10254	0.18961	0.31592
CaI_2	0.12545	0.25067	0.33836
SrF_2	0.06856	0.13784	0.21792
$SrCl_2$	0.09607	0.18807	0.25743
$SrBr_2$	0.11431	0.20412	0.28559
SrI_2	0.12684	0.25358	0.38586
BaF_2	0.06999	0.13965	0.20357
$BaCl_2$	0.09923	0.19828	0.29738
$BaBr_2$	0.10743	0.21475	0.35789
BaI_2	0.14028	0.22743	0.38660

TABLE VI

Observed and calculated polarizabilities in 10^{-25} cm^3 for the dihalides of some group IIA elements

Molecule	$\Sigma\alpha_{\parallel p}$	$\Sigma 2\alpha_{\perp}$	$\Sigma\alpha_{\parallel n}$	α_M(calcd)	α_M(obsd)
BeF_2	5.833	42.455	8.400	18.896	16.167
$BeCl_2$	31.907	99.373	23.794	51.691	
$BeBr_2$	47 450	130 472	33.274	70 399	
BeI_2	78 487	185.917	50.949	105.118	
MgF_2	8 834	49 218	8.400	22.151	18.426
$MgCl_2$	50 409	113 278	23 794	62 494	53 851
$MgBr_2$	76.794	147.732	33.274	85.933	
MgI_2	122.923	210.336	50.949	128.069	
CaF_2	11 746	56.647	8 400	25.598	24 964
$CaCl_2$	69 922	127 768	23.794	73.828	
$CaBr_2$	99 921	165 147	33.274	99.447	
CaI_2	164.632	233.893	50.949	149.825	
SrF_2	14 019	61.676	8.400	28.032	30.195
$SrCl_2$	81.456	136 503	23.794	80.584	70.126
$SrBr_2$	121.547	175.097	33.274	109.973	
SrI_2	197.356	246.187	50.949	164.831	
BaF_2	19 991	65.089	8.400	31.160	38.516
$BaCl_2$	93 753	143 212	23.794	86.919	79.806
$BaBr_2$	132.460	183 194	33.274	116.309	
BaI_2	215.809	257.234	50.949	174.664	

The molecular polarizability is composed of mainly from bond parallel and bond perpendicular components. The bond parallel component is obtained from the contributions of two sources, namely, bond region electrons and nonbond region electrons according to the valence bond interpretation. The contribution to the parallel component by the bond region electrons is calculated using a linear combination of atomic delta-function wave functions representing the two nuclei involved in the bond from the following expression given as $\alpha_{\parallel_b} = 4nA_{12}(1/a_0)(<x^2>)^2$ where n is the bond order, A_{12} the root mean-square delta function strength of the two nuclei involved in the bond, a_0 the radius of the first Bohr orbit of atomic hydrogen and $<x^2>$ the mean-square position of a bonding electron which may be expressed as $<x^2> = (R^2/4)+(1/2cR_{12}^2)$ where R is the internuclear distance at the equilibrium configuration. In the case that the bond is of the heteronuclear type, a polarity correction is necessary to produce the ionic character believed to exist and then the expression for the parallel component of the polarizability is written as $\alpha_{\parallel_p} = \alpha_{\parallel_b}\sigma$ where $\sigma = \exp[-(1/4)(X_1-X_2)^2]$. Here X is Pauling's electronegativity (1960). The calculated values of the sum of the bond parallel components, $\Sigma\alpha_{\parallel_p}$ in 10^{-25} cm^3 by the bond region electron for all the molecules are given under the second column of Table VI. The contribution to the parallel component by the nonbond region electrons is calculated from the expression $\alpha_{\parallel_n} = f_j\alpha_j$ where f_j is the fraction of electrons in the valence shell of the j-th atom not involved in bonding and α_j the atomic polarizability of the j-th atom obtainable from the delta-function strength A_j. In a molecule of the present study, the valence electrons of the central atom are completely shared in bonding while there are six valence electrons are left unshared on each end atom. The calculated values of the sum of the bond parallel components, $\Sigma\alpha_{\parallel_n}$ in 10^{-25} cm^3 by the nonbond region electrons for all the molecules are given under the fourth column of Table VI. Thus the contributions by the bond region electrons as well as nonbond region electrons to the parallel component of the polarizability are clearly distinguished.

The perpendicular component of a diatomic molecule is assumed to be the sum of the two atomic polarizabilities, i.e. $\alpha_\perp = 2\alpha_A$ for a nonpolar diatomic molecule, A_2, $= 2(X_A^2\alpha_A+X_B^2\alpha_B)/(X_A^2+X_B^2)$ for a molecule $A-B$ where X stands for the electronegativity on the Pauling scale and α for the atomic polarizability. Extending this principle, the sum of the perpendicular components of all the bonds in a polyatomic molecule is given as $\Sigma 2\alpha_\perp = n_{df}(\Sigma X_j^2\alpha_j)/(\Sigma X_j^2)$ where n_{df} is the number of residual atomic polarizability degrees of freedom and the other quantities are known. The number of residual atomic polarizability degrees of freedom is obtained directly from the structure of a molecule. Every isolated atom is allowed to possess three atomic polarizability degrees of freedom, and every bond which is formed between two atoms removes two of three degree of freedom, with the exception that (1) if two bond are formed from the same atom and exist in a linear configuration, then only three atomic polarizability degrees of freedom

are lost, and (2) if three bonds are formed from the same atom and exist in a plane, then only five atomic polarizability degrees of freedom are lost. Extending this principle, a linear molecule of the present study has only six residual atomic polarizability degrees of freedom (see Fig. 1). The calculated values of the sum of the perpendicular components, $\Sigma 2\alpha_{\perp}$ in 10^{-25} cm^3 for all the molecules are given under the third column of Table VI

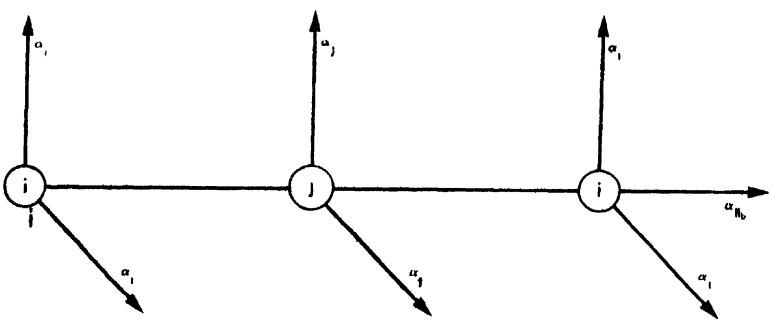

Fig. 1. Residual atomic polarizability degrees of freedom for a linear symmetrical triatomic molecule.

The average or mean molecular polarizability is obtained from the following expression $\alpha_M = (1/3)(\Sigma\alpha_{\parallel_p} + \Sigma\alpha_{\parallel_v} + \Sigma 2\alpha_{\perp})$ The calculated values of the molecular polarizabilities in 10^{-25} cm^3 for all the molecules are given under the fifth column of Table VI. The experimental values of molar refractions given by Batsanov (1961) for some of the molecules of present study were substituted into the Lorentz-Lorentz equation to obtain the molecular polarizabilities and their values in 10^{-25} cm^3 are given under the sixth column of Table VI. It is seen what the calculated molecular polarizabilities are in good agreement with the available experimental values Thus the present investigation further testifies that the delta-function potential model enables us to evaluate the bond and molecular polarizabilities not only for non-metals but also for metals, thereby establishes that it is the most satisfactory one among the various models so far developed.

In considering various potential models so far developed, they have been very limited to atoms, ions and simple diatomic systems but not been extended to even simple polyatomic molecules and may be observed from the following: Hasse (1930, 1931) evaluated the polarizabilities for the helium atom and lithium ion by using the Lennard-Jones 6-12 potential model involving several types of ground state as well as perturbed state wave functions in terms of the perturbing potential. Hirschfelder (1935) computed the polarizabilities of molecular hydrogen and the diatomic hydrogen ion by applying the variational method of Hylleraas (1930) and Hasse (1930, 1931) upon the eigenfunctions proposed by Rosen (1931) and Wang (1928). It was found that the Kirkwood (1932) formula was applicable to the diatomic hydrogen ion and polarizabilities were obtained for may

internuclear separations by using the eigenfunction developed by Guillemin and Zener (1929). The calculated values by Hirschfelder (1935) were compared with those of Mrowka (1932) and Steensholt (1935) but they are not in good agreement with each other. Van Vleck (1932) and Atanasoff (1930) pointed out from their investigations that the Hylleraas method (1930) is not strictly applicable to approximate eigenfunctions and may yield results either too small or too large. The approach of Buckingham (1937) based on the Kirkwood's variational method (1932) and involved heavier atoms leads to complex determinental self-consistent field wave functions from his calculations of atomic polarizabilities for Ne, Na^+, Cl^-, *A*, K^+, Kr and Cs^+ Bell and Long (1950) calculated the polarizabilities of H_2^+ and H_2 molecules from six different unperturbed wave functions but the results are not sensitive to the wave functions adopted, especially for the unperturbed molecules. Abbott and Bolton (1952 1953) studied H_2^+, H_2 and N_2 molecules and used the polarizability as a criterion for determining the molecular wave function of a system by a self-consistent field method Kolker and Karplus (1963) calculated the electric polarizability tensor $\bar{\alpha}$ with "*ab initio*" wave functions for a series of first row diatomic molecules such as H_2, Li_2 N_2, LiH HF LiF and CO Since these methods have not been extended to polyatomic molecules such calculations have not been carried out here to make a comparison with the results of delta-function potential model and the experimental values On studying all the potential models so far developed the delta-function potential provides the feasibility of obtaining explicit expression for the parallel and perpendicular components and the mean polarizabilities for the diatomic as well as polyatomic systems The sum of the perpendicular components of all the bonds in a molecule $\Sigma 2\alpha_\perp$ is a linear combination of atomic polarizabilities and is independent of the internuclear distance whereas the bond parallel component is dependent on the internuclear distance. Hence the perpendicular component will always be transferable from one molecular system to another having similar chemical bonds irrespective of the accuracy in the values of the internuclear distances in both systems but such a transfer in the case of parallel component would be possible only when the internuclear distances are nearly identical in the two systems considered Since the nonbond region electrons also contribute to the parallel component such a transfer would be possible for the bods formed by the atoms with identical lone pairs of electrons From the previous investigations as well as with the present one it is felt that the delta-function potential model is a very satisfactory one for such calculations of bond and molecular polarizabilities and a further work on this aspect for various polyatomic molecules having their elements from the B-group is in progress

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